



Degradation and environmental risk of surfactants after the application of compost sludge to the soil

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ABSTRACT

In this work, the degradation of anionic and non-ionic surfactants in agricultural soil amended with sewage sludge is reported. The compounds analysed were: linear alkylbenzene sulphonates (LAS) with a 10–13 carbon alkylic chain, and nonylphenolic compounds (NPE), including nonylphenol (NP) and nonylphenol ethoxylates with one and two ethoxy groups (NP1EO and NP2EO). The degradation studies were carried out under winter (12.7 °C) and summer (22.4 °C) conditions in Andalusia region. The concentration of LAS was reduced to 2% of the initial concentration 100 day after sludge-application to the soil. The half-life time measured for LAS homologues were ranged between 4 and 14 days at 12.7 °C and between 4 and 7 days at 22.4 °C.

With regard to NPE compounds, after 8 and 4 days from the beginning of the experiment at 12.7 and 22.4 °C, respectively, their concentration levels were increased to 6.5 and 13.5 mg/kg dm (dry matter) as consequence of the degradation of nonylphenol polyethoxylates. These concentration levels were reduced to 5% after 63 and 70 days for 12.7 °C and 22.4 °C, respectively. The half-life times measured for NPEs were from 8 to 16 days at 12.7 °C and from 8 to 18 days at 22.4 °C.

Environmental risk assessment revealed that for LAS homologues no environment risk could be expected after 7 and 8 days of sludge application to the soil for 22.4 and 12.7 °C, respectively; however, potential toxic effects could be observed for the nonylphenolic compounds during the first 56 days after sludge application to the soil.

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1. Introduction

Nowadays, more than 8 million of tonnes of sewage sludge are generated as results of wastewater treatment processes (Magoarou, 2000). Therefore, it is essential to ensure non-pollutant and economical removal of sludge, or its recovery in a rational manner. In the European Community, the most widely used solutions are: controlled transport to dumps, application to farmlands, incineration, application to impoverished soils and recovery of energy or mineral products. The application of sewage sludge to the soil seems to be the best option since not only improve the quality of the degraded soil but also it is included in the paradigm of reutilization, which implies an economic value for this by-product of wastewater treatment. In the European Union, around 4 million of tonnes of dry sludge are applied yearly to the land (EU, 2008). However, the presence in sludge of potentially hazardous substances such as heavy metals and some organic compounds constitutes the main problem in the application of the sludge to the soil (Abad et al., 2005; Alonso et al., 2002).

In order to improve the present situation for sludge management and reduce presence of pollutants in the soil, European Union published the third draft of a future Sludge Directive entitled “Working Document on Sludge” (CEC, 2000), where concentration limit values for some organic compounds are included for the first time in the EU regulations.

Since the publication of this text several studies has been reported in the literature about the presence and distribution of the organic compounds included in the future EU Directive during the sludge management processes (Abad et al., 2005; Aparicio et al., 2009; González et al., 2010a; Pakou et al., 2009; Soares et al., 2008). In these studies the surfactants linear alkylbenzene sulphonates (LAS) and nonylphenol ethoxylates (NPE, sum of nonylphenol, nonylphenol mono- and diethoxylate) are shown as some of the most problematic compounds in the application of sewage sludge to the soil according with concentration levels found in sludge and limit values fixed by the future EU Directive (Abad et al., 2005; Aparicio et al., 2009; Eriksson et al., 2008; Pakou et al., 2009).

In spite of the numerous studies carried out about the presence and distribution of these compounds in sludge, few studies have been reported in the literature about their distribution and fate after the application of sewage sludge to the soil (Gómez-Rico et al., 2008; Petersen et al., 2003). As consequence, there is a lack

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of information about their occurrence in soil and about the potential ecotoxicological risk associate to the application of these sludges to the soil.

The purposes of this study were to investigate the fate of the surfactants linear alkylbenzene sulphonates (LAS: C10, C11, C12 and C13) and nonylphenol compounds (NPE: nonylphenol, nonylphenol mono- and diethoxylate) in sludge-amended soil and evaluate the environmental risk caused by the application of the sludge onto soil.

2. Experimental

2.1. Chemicals and reagents

HPLC grade acetone, acetonitrile, methanol and water were purchased from Romil Ltd. (Barcelona, Spain). Commercial LAS mixture containing C₁₀-LAS (12.3%), C₁₁-LAS (32.1%), C₁₂-LAS (30.8%) and C₁₃-LAS (23.4%) was supplied by Petroquímica Española (PETRESA). NP Pestanal[®] technical grade was obtained from Riedel-de-Haën (Seelze, Germany), NP1EO and NP2EO Igepal[®] CO-210 technical mixture was obtained from Aldrich (Milwaukee, WI, USA).

Three-millilitres solid phase extraction (SPE) cartridges, packed with 60 mg of OASIS MCX, were purchased from Waters (Milford, MA, USA).

Stock solutions of each of the studied compounds at concentration levels of 1000 mg/L were prepared in methanol and stored at 4 °C. Working solutions were prepared by diluting the stock standard solutions in a methanol:water mixture (1:1, v/v).

2.2. Compost, soil and compost-amended soil samples

Compost samples were collected from a composting plant sited in Seville (South of Spain) where anaerobically-digested and dehydrated sludge from four urban wastewater treatment plants are treated. Composting process is based on natural composting of anaerobically-digested and dehydrated sludge in dynamic batteries thermally controlled and with aeration facilitated by turning.

Soil samples were collected from an agricultural land sited in Seville. The soil was Mediterranean type, with a thick sand content of 72.6%, fine sand: 4.5%, slime: 4.1%, clay: 18.8% and organic carbonate: 0.2%.

Previously to the application of compost to the soil, both samples were characterised (Tables 1 and 2).

2.3. Experimental design

The experiments were carried out during a period of 100 days. Two temperature values were tested: 12.7 and 22.4 °C, corresponding to the mean temperature during winter and summer period, respectively, in the Mediterranean region of Andalusia (South of Spain). Irradiation levels of 1091 W/m² and humidity conditions of 33% were fixed in all experiments.

For each temperature value, five reactors of glass (diameter 10 cm), filled with 500 g of a sludge:soil mixture 5:95 (corresponding approximately to 170 T/ha), and two controls, filled with 500 g of soil, were used. The mixture was homogenised by hand before filling the reactor to achieve a mixture similar to the application of sludge in a full scale agricultural soil. 20% of humidity in each reactor was achieved by adding 100 mL of deionised water.

Thirty samples (2.0 g) were collected from each reactor as follows: five weekly samples were collected during first 15 days; three weekly samples from days 16 to 45, two weekly samples from the days 46 to 53 and a weekly sample from days 54 to 100.

Samples were lyophilised in a cryodos-50 (Telstar, Terrasa, Spain) lyophilizer, sieved (particle size <2 mm) and stored at −30 °C until analysis.

Table 1

Physical and chemical characteristics of compost.

Parameter	Value
pH	6.51
Dryness (%)	80.1
Ashes (%)	79.9
Nitrogen (% TKN)	1.74
Carbon (%)	14.4
Relation C/N	8.25
Organic material (%)	24.8
Calcium (% CaO)	1.77
Magnesium (% MgO)	0.48
Assimilable phosphorus (% P ₂ O ₅)	0.63
Total phosphorus (% P ₂ O ₅)	4.80
Assimilable potassium (% K ₂ O)	0.27
Total potassium (%K ₂ O)	1.09
Conductivity (mS/cm)	5.09
<i>Escherichi coli</i> (NMP/g)	19
Salmonella (en 25 g)	Absence

Table 2

Physical and chemical characteristics of the soil.

Parameter	Value
Texture	Loam-sand
Coarse sand (%)	72.6
Thin sand (%)	4.5
Silt (%)	4.1
Clay (%)	18.8
Carbonate (% CaCO ₃)	1.6
Oxidise organic carbon (%)	0.207
Oxidise organic material (%)	0.36
Organic nitrogen estimate (%)	0.027
Relation C/N	7.53
pH	8.75
Specific surface area	19.5
Volume of micro + mesopores ($r_p < 250 \text{ \AA}$) (mm ³ /g)	29.0
Volume of macropores ($250 \text{ \AA} < 40 \text{ \mu m}$) (mm ³ /g)	126.4

2.4. Analysis of organic compounds

LAS and NPE were simultaneously extracted from compost and sludge-amended soil samples by sonication assisted extraction as it is described in a previously reported method (González et al., 2010b).

Chromatographic analysis was performed using an HPLC 1100 Series instrument (Agilent, USA) equipped with an ultraviolet diode array (DAD) and rapid scan fluorescence (FI) detector connected on line. Separations were carried out using an Inertsil Ph-3 (150 mm × 4.6 mm i.d., 5 μm) column (GL Sciences, Inc., Tokio, Japan) protected by an Inertsil Ph-3 (4 mm × 10 mm i.d., 5 μm) guard column (GL Sciences, Inc., Tokio, Japan). Analytes were separated by gradient elution as previously is reported (González et al., 2010b). Recoveries achieved with the applied method were from 78% to 103%, and limit of detection and quantification were ranged 0.01–0.03 and 0.03–0.10 mg/kg dm, respectively.

2.5. Environmental risk assessment

The ecotoxicological risk was evaluated using risk quotients (RQs) as previously is reported by González et al. (2010a). RQs were determined as the ratio between the concentrations measured in soil for LAS homologues (C10, C11, C12 and C13) and nonylphenolic compounds (NP, NP1EO and NP2EO) and the predicted non-effect concentration (PNEC) of each compound, which is the concentration for which no adverse effect is suspected to occur. RQ for LAS (sum of C10, C11, C12 and C13) and NPE (sum of NP, NP1EO and NP2EO) were determined too.

$PNEC_{water}$ values are derived from acute toxicity data from literature (lethal concentration, LC; effect concentration, EC; and non-observed effect concentration, NOEC) obtained from toxicological studies in each environmental compartment (Fenner et al., 2002; Van Vlaardingen et al., 2003) applying an assessment factor of 1000 which depends on the available toxicity data (ECB, 2003).

$PNEC_{soil}$ were derived from $PNEC_{water}$, assuming that the sensitivity of aquatic organisms is comparable to that of organisms living in soil or sediment and applying the equilibrium partition theory as it is suggested by Van Vlaardingen et al. (2003):

$$PNEC_{soil} = PNEC_{water} \times K_d \quad (1)$$

where $PNEC_{soil}$ is the predicted no-effect concentration in soil, $PNEC_{water}$ is the PNEC value obtained in water compartment, K_d is the soil–water partition coefficient.

The individual partition coefficients were related to the organic carbon content of the respective soils by the following equation:

$$K_d = K_{oc} \times f_{oc} \quad (2)$$

where K_{oc} represents the organic carbon partition coefficient and f_{oc} the organic carbon fraction in soil. Log K_{oc} values of 4.02, 3.90, 4.83, and 3.39 were applied for LAS C10, C11, C12 (Ying, 2006) and C13 (Feijtel et al., 1999), respectively, and values of 3.97, 4.94 and 5.06 were used for NP (Düring et al., 2002), NP1EO and NP2EO (Yu et al., 2008) respectively. f_{oc} values of 0.02 g/kg was applied for normalised to EU standard soil (Van Vlaardingen et al., 2003).

3. Results and discussion

3.1. Concentrations of surfactants in compost and soil samples

Previously to the application of compost to the soil, both samples were analysed for the determination of the concentration levels of LAS and NPE. Concentrations measured are shown in Table 3.

In compost samples, higher concentrations were found for LAS homologues (mean concentration 171 mg/kg dm (dry matter)). NPE were found at mean concentration levels of 22.4 mg/kg dm. The studied compounds were not detected in soil samples.

After sludge application to the soil, concentration levels of LAS homologues and NPE decreased substantially being found at concentration levels up to 6.64 and 0.66 mg/kg dm, respectively. This fact indicates that even at concentration levels in compost samples lower than those fixed by the future EU Directive (2600 mg/kg dm for LAS and 50 mg/kg dm for NPE), surfactant are still found in sludge-amended soil at concentration levels of several µg or even mg per kilogram (Table 3).

3.2. Degradation of organic compounds

3.2.1. LAS degradation

The highest concentration of LAS homologues was found for LAS C11, followed by LAS C12, C10 and C13, in that order. For both temperatures (12.7 and 22.4 °C) a rapid degradation of LAS was observed. The half-life times ($t_{1/2}$) were from 4 (C12) to 14 (C11) days at 12.7 °C and from 4 (C12) to 7 (C11) days in experiments carried out at 22.4 °C (Table 4).

Both experiments a high influence of temperature was observed during experimental time (Fig. 1). This fact was more severe in the case of C11 for which the half-life observed at 12.7 °C was reduced to the half in the case of the experiment carried out at 22.4 °C. In spite of that, LAS homologue C11 was the compound with the highest persistence (present after 49 and 39 days at 12.7 and 22.4 °C, respectively), followed by the homologues C13 (Fig. 1), C12 and C10, in that order. This distribution could be explained by the highest retention capacity into the soil for these homologues with

Table 3

Mean concentration levels of surfactants in sludge, soil and sludge-amended soil ($n = 10$).

Compounds		Sludge (mg/kg dm)	Soil (mg/kg dm)	Sludge-amended soil (mg/kg dm)
LAS	C10	57.9	<LOD	4.17
	C11	157	<LOD	6.64
	C12	275	<LOD	4.44
	C13	196	<LOD	3.53
	Σ LAS	686	<LOD	18.8
NPEs	Average LAS	171	<LOD	4.70
	NP2EO	30.3	<LOD	0.57
	NP1EO	17.5	<LOD	0.66
	NP	19.3	<LOD	0.27
	Σ NPEs	67.1	<LOD	1.50
	Average NPEs	22.4	<LOD	0.50

<LOD: lower than the limit of detection of the method.

Table 4

Half-life time ($t_{1/2}$) of surfactants measured in degradation experiments.

Compound		Temperature	
		12.7 °C (days)	22.4 °C (days)
LAS	C10	7	6
	C11	14	7
	C12	4	4
	C13	7	6
NPEs	NP2EO	16	8
	NP1EO	8	9
	NP	16	18

longer alkyl chain and, as consequence, the minor availability for the biodegradation. The high persistence of the homologue C11 at both temperatures could be due to the high concentration level found at the beginning of the experiment.

Mean concentration levels of LAS (sum of C10, C11, C12 and C13) of 18.0 and 19.5 mg/kg dm for experiments at 12.7 and 24.5 °C, respectively, were found in sludge-amended soil samples at the beginning of the experiment (Fig. 2). The concentration of LAS (sum of C10, C11, C12 and C13) was reduced to 5% of the initial concentration 49 and 21 days after sludge-application to the soil at 12.7 and 22.4 °C. The observed degradation could be divided in two phases. In the first phase (1–21 and 1–16 days for 12.7 and 22.4 °C, respectively) a rapid degradation was observed. During this phase the concentration of LAS was reduced to 25% and 9% of the initial concentration, respectively, for 12.7 and 22.4 °C. During the second phase (from 22 to 90 days at 12.7 °C and from 17 to 90 days at 22.4 °C) a slow degradation was observed. During this phase initial concentration of LAS was reduced to 1.87% and 0.41%, respectively.

3.2.2. NPE degradation

After sludge application to the soil, nonylphenolic compounds were present at mean concentration levels of 0.81, 1.00 and 0.27 mg/kg dm in the experiment at 12.7 °C and of 0.33, 0.33 and 0.27 mg/kg dm in experiment carried out at 22.4 °C, for NP2EO, NP1EO and NP, respectively (Fig. 3). The half-life measured for NPE was influenced by the number of ethoxylated groups as well as the temperature (Table 4). In all cases, an increase of concentration was observed in a few days from the beginning of the experiment. These could be explained by the degradation of polyethoxylated compounds present in compost, whose main degradation products are NP2EO, NP1EO and NP (Gómez-Rico et al., 2008). No influence of temperature was observed in the degradation of nonylphenol ethoxylates, except in the case of NP2EO. This fact was faster in experiment carried out at 22.4 °C and, as consequence, at this

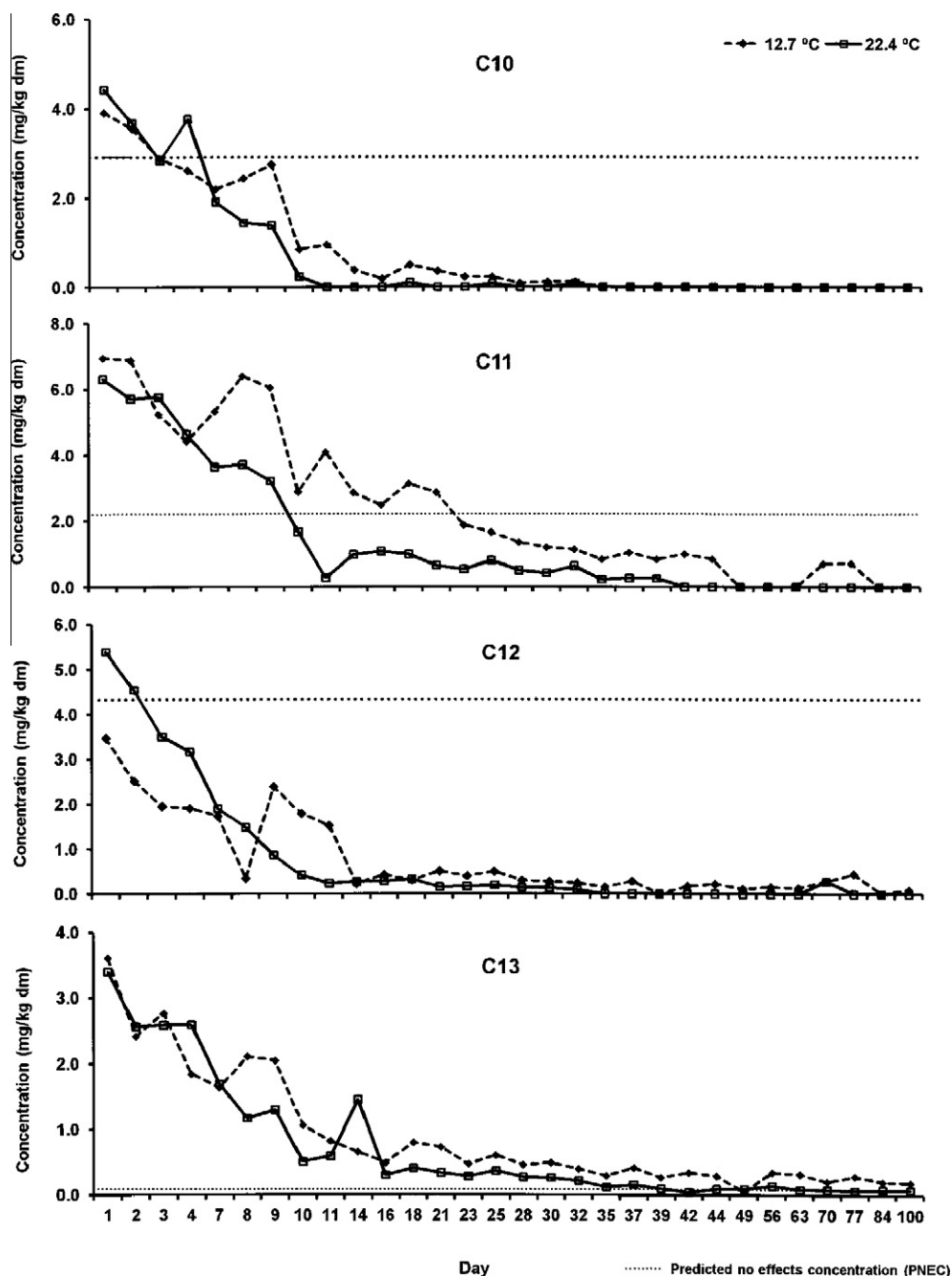


Fig. 1. Concentration levels of LAS homologues measured in sludge-amended soil during degradation experiment ($n = 5$).

temperature the increase of concentration levels was observed during the first 4 days of experiment while at 12.7 °C this increase was observed during the first 8 days of the experiment. A high reduction was observed for the half-life measured for NP2EO from 12.7 to 22.4 °C while no reduction was observed for NP1EO and NP (Table 4). This could be explained through the higher persistence of the compound with lower number of ethoxylates groups.

Mean concentration levels of NPE (sum of NP2EO, NP1EO and NP) measured at the beginning of the experiment were of 2.09 and 0.83 mg/kg dm for the experiment carried out at 12.7 and 22.4 °C, respectively (Fig. 4). The same temperature effect observed for the individual compounds was reproduced in the case of NPE. After 8 and 4 days from the beginning of the experiment for 12.7 and 22.4 °C concentration levels of NPE was increased to 6.5 and

13.5 mg/kg dm, respectively. These concentration levels were reduced to 5% after 63 and 70 days, respectively.

3.3. Environmental risk assessment

3.3.1. Toxicity data of organic compounds

The toxicity of LAS homologues was seriously influenced by the length of alkyl chain. Several studies show the wide variety in the LAS toxicity from one species to the next and even between organisms from the same species, especially in the case of algae. This fact could be due to the different experimental design and the wide range of sensitive species used in the determination of the toxicity data, referring not only to the LAS homologues but also the sum of LAS C10, C11, C12 and C13.

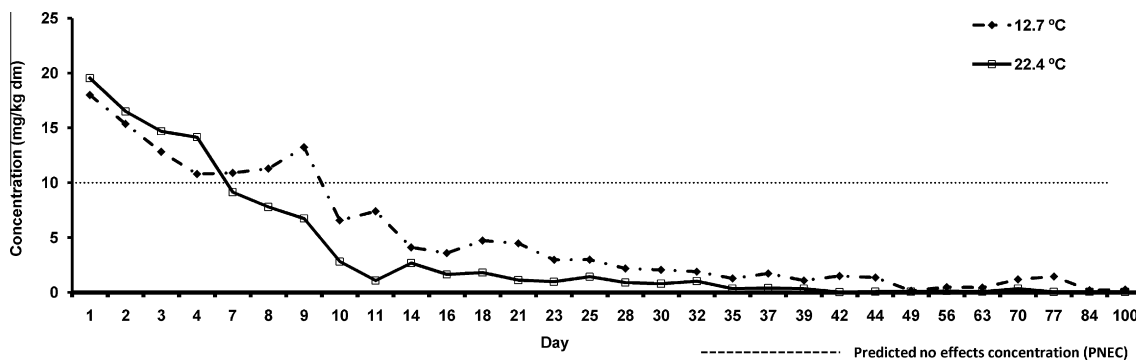


Fig. 2. Concentration levels of LAS (sum of C10, C11, C12 and C13) in sludge-amended soil during degradation experiment ($n = 5$).

Chronic effects have been observed for *Daphnia magna* at concentration levels from 3.35 (C13) to 13.9 mg/L (C10). In the case of LAS (sum of C10, C11, C12 and C13), most studies carried out showed an increase in the toxicity in relation to those found for LAS homologues (Table 5).

With regard to nonylphenol ethoxylates, the toxicity data found in the literature showed an increase in the toxicity for these compounds with the decrease of the number of ethoxy groups (Table 6). For NP, the toxicity data found in the literature were from 20.7 to 157 $\mu\text{g/L}$ (Brooke, 1993; Fenner et al., 2002; TenEyck and Markee,

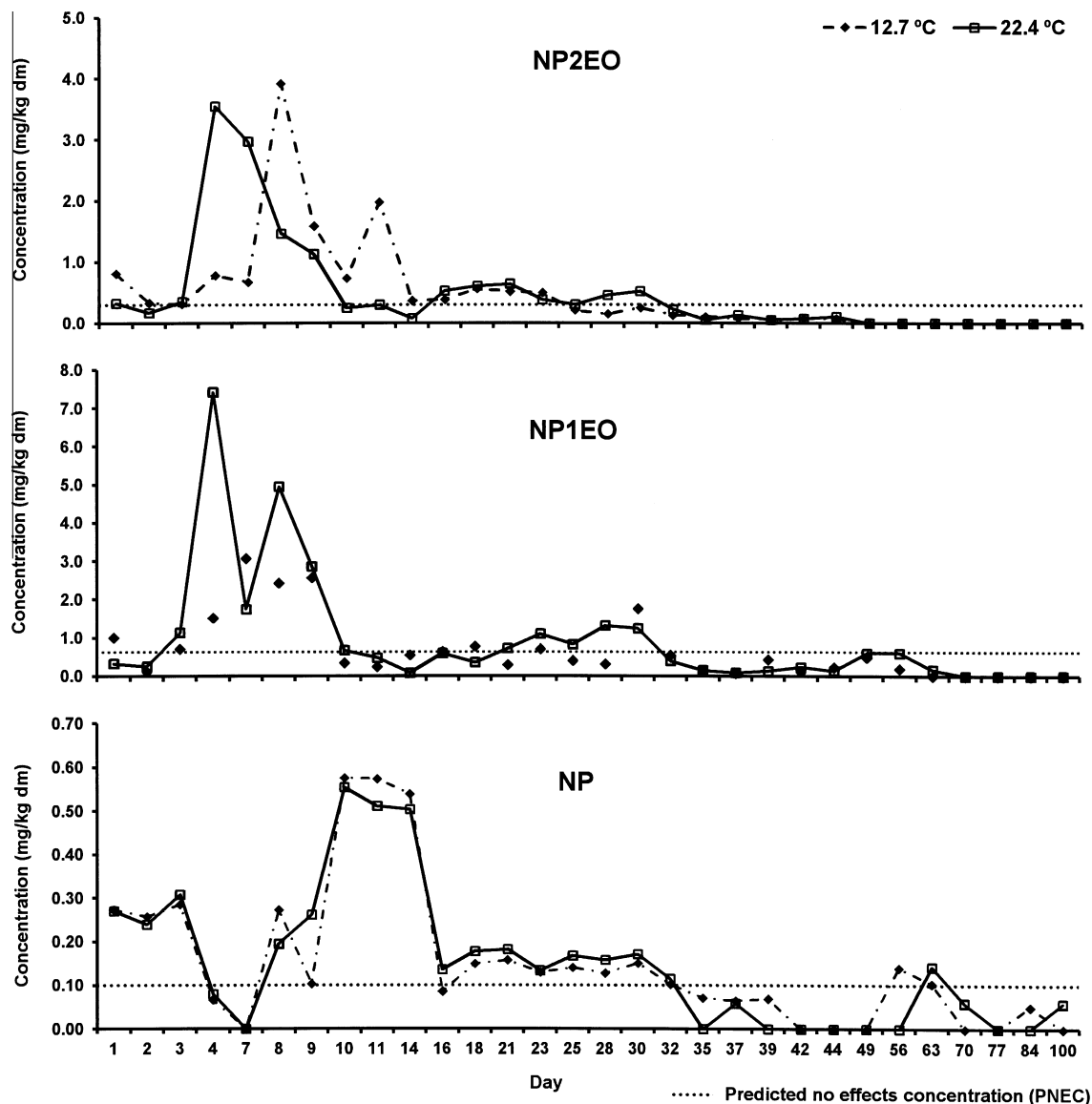


Fig. 3. Concentration levels of NP2EO, NP1EO and NP measured in sludge-amended soil samples during degradation experiment ($n = 5$).

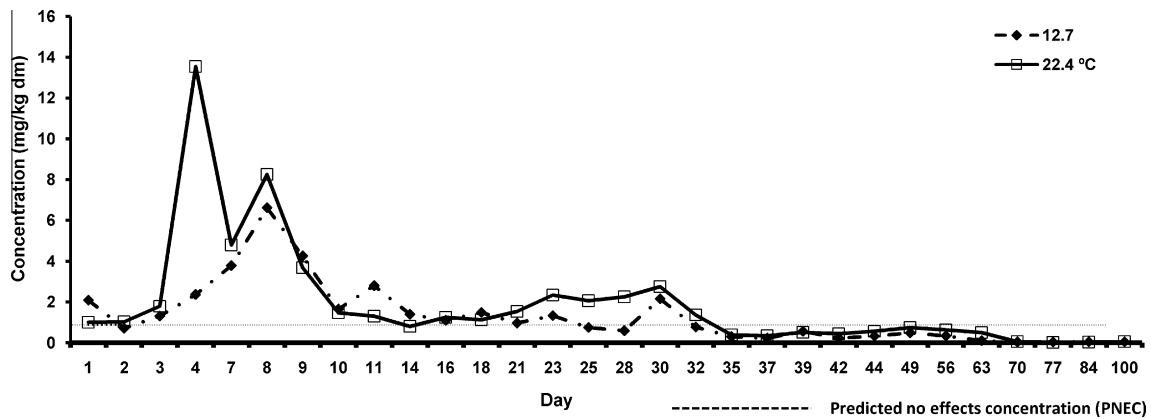


Fig. 4. Concentration levels of NPE (sum of NP2EO, NP1EO and NP) in sludge-amended soil during degradation experiment ($n = 5$).

Table 5

Acute toxicity data of linear alkylbenzene sulphonates.

Compound	Specie	Test	Aquatic organisms (mg/L)	Terrestrial organisms (mg/kg)	References
LAS	C10	<i>Daphnia magna</i> (crustacean)	EC ₅₀ , 48 h	16.7	HERA (2009)
		<i>Daphnia magna</i> (crustacean)	LC ₅₀ , 48 h	13.9	Ying (2006)
		<i>Pimephales promelas</i> (fish)	LC ₅₀ , 48 h	39.6	HERA (2009)
	C11	<i>Tetraselmis suecica</i> (algae)	EC ₅₀ , 72 h	13.37	Garrido-Pérez et al. (2008)
		<i>Isochrysis aff. galbana</i> (algae)	EC ₅₀ , 72 h	7.70	Garrido-Pérez et al. (2008)
		<i>Nannochloropsis gaditana</i> (algae)	EC ₅₀ , 72 h	1.38	Garrido-Pérez et al. (2008)
		<i>Daphnia magna</i> (crustacean)	EC ₅₀ , 48 h	9.2	HERA (2009)
		<i>Pimephales promelas</i> (fish)	LC ₅₀ , 48 h	19.8	HERA (2009)
	C12	<i>Daphnia magna</i> (crustacean)	CL ₅₀ , 48 h	8.1	Ying (2006)
		<i>Daphnia magna</i> (crustacean)	EC ₅₀ , 48 h	4.8	HERA (2009)
		<i>Pimephales promelas</i> (fish)	EC ₅₀ , 48 h	3.2	HERA (2009)
	C13	<i>Rhodomonas salinas</i> (algae)	EC ₅₀ , 72 h	0.36	Garrido-Pérez et al. (2008)
		<i>Isochrysis aff. galbana</i> (algae)	EC ₅₀ , 72 h	0.53	Garrido-Pérez et al. (2008)
		<i>Nannochloropsis gaditana</i> (algae)	EC ₅₀ , 72 h	0.18	Garrido-Pérez et al. (2008)
		<i>Daphnia magna</i> (crustacean)	EC ₅₀ , 48 h	2.35	HERA (2009)
		<i>Pimephales promelas</i> (fish)	EC ₅₀ , 48 h	1.04	HERA (2009)
Σ LAS	<i>Navicula peliculosa</i> (algae)	EC ₅₀ , 96 h	1.4	–	Garrido-Pérez et al. (2008)
	<i>Arcatia tonsa</i> (crustacean)	EC ₅₀ , 48 h	1.11	–	Garrido-Pérez et al. (2008)
	<i>Pleuronectes plateas</i> (fish)	EC ₅₀ , 96 h	1	–	Garrido-Pérez et al. (2008)
	<i>H. ulvae</i> (molluscan)	LC ₅₀ , 96 h	–	141	Hampel et al. (2007)
	<i>Enchytraeus crypticus</i> (invertebrate)	NOEC, 28 days	–	120	Krogh et al. (2007)

Table 6

Acute toxicity data of nonylphenol ethoxylates.

Compound	Specie	Test	Aquatic organisms (μg/L)	Terrestrial organisms (mg/kg)	References
NPE	NP	<i>Pimephales promelas</i> (fish)	LC ₅₀ , 96 h	136	TenEyck and Markee (2007)
		<i>Ceriodaphnia dubia</i> (crustacean)	LC ₅₀ , 48 h	92.4	TenEyck and Markee (2007)
		<i>Mysidopsis bahia</i> (crustacean)	LC ₅₀ , 96 h	20.7	Fenner et al. (2002)
		<i>Daphnia magna</i> (crustacean)	LC ₅₀ , 48 h	157	US EPA (2005)
		<i>Daphnia magna</i> (crustacean)	LC ₅₀ , 48 h	104	Brooke (1993)
	NP1EO	<i>Pimephales promelas</i> (fish)	LC ₅₀ , 96 h	218	TenEyck and Markee (2007)
		<i>Ceriodaphnia dubia</i> (crustacean)	LC ₅₀ , 48 h	328	TenEyck and Markee (2007)
		<i>Mysidopsis bahia</i> (crustacean)	LC ₅₀ , 48 h	110	Fenner et al. (2002)
	NP2EO	<i>Pimephales promelas</i> (fish)	LC ₅₀ , 96 h	323	TenEyck and Markee (2007)
		<i>Ceriodaphnia dubia</i> (crustacean)	LC ₅₀ , 48 h	716	TenEyck and Markee (2007)
		<i>Mysidopsis bahia</i> (crustacean)	LC ₅₀ , 48 h	110	Fenner et al. (2002)
		<i>Ceriodaphnia dubia</i> (crustacean)	EC ₅₀ , 96 h	626	Staples et al. (1998)
		<i>Ceriodaphnia dubia</i> (crustacean)	LC ₅₀ , 96 h	1016	Staples et al. (1998)
		<i>Ceriodaphnia dubia</i> (crustacean)	NOEC, 7 days	285	Staples et al. (1998)
		<i>Daphnia magna</i> (crustacean)	LC ₅₀ , 48 h	148	Staples et al. (1998)
	Σ NPEs	<i>Pimephales promelas</i> (fish)	LC ₅₀ , 96 h	190	TenEyck and Markee (2007)
		<i>Ceriodaphnia dubia</i> (crustacean)	LC ₅₀ , 48 h	359	TenEyck and Markee (2007)
		<i>Xenopus Laevis</i> (amphibious)	LC ₅₀ , 96 h	4800	Mann and Bidwell (2000)
		<i>Litoria adelaidensis</i> (amphibious)	LC ₅₀ , 140 h	9200	Mann and Bidwell (2000)
		<i>Crinia insignifera</i> (amphibious)	LC ₅₀ , 135 h	6400	Mann and Bidwell (2000)

2007; US EPA, 2005). While for NP1EO and NP2EO, a few studies have been found in the literature reporting toxicity data in both aquatic and terrestrial organism. Staples et al. (1998) reported LC50 values of 620 µg/L for *Ceriodaphnia dubia* exposed to NP2EO. Studies carried out for TenEyck and Markee (2007) found LC50 values of 716 and 328 µg/L for NP1EO and NP2EO, respectively, using *C. dubia* as target organism (Table 6).

Moreover, synergic effects have been observed in species exposed to NPE mixtures, as consequence, lower toxicity data such as 87, 60 and 42 µg/L, for NP2EO, NP1EO and NP, have been found using *Pimephales promelas* as target organism (TenEyck and Markee, 2007).

Environmental risk assessment in sludge-amended soil was carried out selecting the lowest value of toxicity data found in the literature for each compound and applying an assessment factor of 1000. $PNEC_{soil}$ were calculated from $PNEC_{water}$ as it is described in Section 2.5.

3.3.2. Environmental risk assessment of LAS

Concentration levels of LAS homologues were lower than $PNEC_{soil}$ values after 23 days from the beginning of the experiment, except in the case of C13 whose effect would be observed after 100 day from the initial time (Fig. 1).

The concentrations measured at 12.7 and 22.4 °C showed similar toxic effects for LAS homologues C10 and C12 while concentration levels of LAS C11 were lower than the $PNEC_{soil}$ value after 23 and 10 days from the application of sludge to the soil for 12.7 and 22.4 °C, respectively.

For LAS C13, in spite of the concentrations measured at 12.7 °C and 22.4 °C were similar, the environmental risk assessment at 22.4 °C showed a decrease of toxicological risk after 39 days while concentration levels measured at 12.7 °C were higher than 0.09 mg/kg ($PNEC_{soil}$) during the experimental time.

With regards to LAS (sum of C10, C11, C12 and C13), the $PNEC$ value were calculated from the NOEC value obtained for Krogh et al. (2007). Concentration levels of LAS were lower than 10 mg/kg after 7 and 8 days of sludge application to the soil for 22.4 and 12.7 °C respectively.

3.3.3. Environmental risk assessment of NPE

Concentration levels of NP2EO, NP1EO and NP were lower than $PNEC_{soil}$ values after 37 days from the application of sludge to the soil (Fig. 4). NP2EO and NP1EO showed similar behaviour and concentration levels lower than $PNEC_{soil}$ values were found after 16 and 18 days from the initial time at 22.4 °C and after 23 and 18 days, respectively, at 12.7 °C.

For NPE, $PNEC_{soil}$ calculated was 0.88 mg/kg. This value showed an increase of the toxicity with regards to the individual compounds. As result, concentration levels measured in sludge-amended soil were higher than this value during the first 56 days of experiment.

4. Conclusions

Degradation of surfactants in soil amended with sewage sludge has been studied during 100 days under cold (12.7 °C) and hot (22.4 °C) conditions. For all studied compounds an influence of the temperature in the degradation was observed during the experiment, being the slowest degradation observed in the experiment carried out at 12.7 °C. The half-life time measured LAS homologues were lower than 14 days at 12.7 °C and lower than 7 days at 22.4 °C and the concentration of LAS (sum of C10, C11, C12 and C13) was reduced to 5% of the initial concentration after 49 and 21 days from the application of the sludge to the soil.

An increase of the concentration levels of nonylphenolic compounds was observed during the first days of the experiment as consequence of the degradation of the nonylphenol polyethoxylate compounds. Concentration levels were reduced to 5% after 63 and 70 days at 12.7 and 22.4 °C.

Environmental risk assessment reveals that after 23 days in the case of LAS and 56 days in the case of NPE potential toxic effects could not be expected, except in the case of LAS C13 whose effect could be expected 100 days after the application of sewage sludge to the soil.

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References

- Abad, E., Martínez, K., Planas, C., Palacios, O., Caixach, J., Rivera, J., 2005. Priority organic pollutant assessment of sludges for agricultural purposes. *Chemosphere* 61, 1358–1369.
- Alonso, E., Callejón, M., Jiménez, J.C., Ternero, M., 2002. Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere* 47, 765–775.
- Aparicio, I., Santos, J.L., Alonso, E., 2009. Limitation of the concentration of organic pollutants in sewage sludge for agricultural purposes: a case of study in south Spain. *Waste Manage. (Oxford)* 29, 1747–1753.
- Brooke, L.T., 1993. Acute and chronic toxicity of nonylphenol to ten species of aquatic organisms, Technical report. US Environmental Protection Agency Environmental Research Laboratory, Duluth, MN.
- CEC, 2000. Working Document on Sludge. 3rd Draft, Brussels 27 April 2000, DG. Environment, p. 18.
- Düring, R.A., Krahe, S., Gath, S., 2002. Sorption behavior of nonylphenol in terrestrial soils. *Environ. Sci. Technol.* 36, 4052–4057.
- ECB (European Chemicals Bureau), 2003. Technical guidance document on risk assessment. Document EUR 20418 EN. European Commission Joint Research Centre, Ispra, Italy. <http://ec.europa.eu/environment/chemicals/exist_subst/pdf/tgdpart2_2ed.pdf>.
- Eriksson, E., Christensen, N., Schmidt, J.E., Ledin, A., 2008. Potential priority pollutants in sewage sludge. *Desalination* 226, 371–388.
- European Union (EU), 2008. European Commission Consultation on the environmental, economic and social impacts of the use of sewage sludge on land.
- Feijtel, T.C.J., Struijs, J., Matthijs, E., 1999. Exposure modelling of detergent surfactants. Prediction of 90th-percentile concentrations in the Netherlands. *Environ. Toxicol. Chem.* 18, 2645–2652.
- Fenner, K., Kooijman, C., Scheringer, M., Hungerbühler, K., 2002. Including transformation products into the risk assessment for chemicals: the case of nonylphenol ethoxylate usage in Switzerland. *Environ. Sci. Technol.* 36, 1147–1154.
- Garrido-Pérez, M.C., Perales-Vargas, J.A., Nebot-Sanz, E., Sales-Márquez, D., 2008. Effect of the test media and toxicity of LAS on the growth of *Isochrysis galbana*. *Ecotoxicology* 17, 738–746.
- Gómez-Rico, M.F., Font, R., Vera, J., Fuentes, D., Disante, K., Cortina, J., 2008. Degradation of organic pollutants in Mediterranean forest soils amended with sewage sludge. *Chemosphere* 71, 2129–2138.
- González, M.M., Martín, J., Santos, J.L., Aparicio, I., Alonso, E., 2010a. Occurrence and risk assessment of nonylphenol and nonylphenol ethoxylates in sewage sludge from different conventional treatment processes. *Sci. Total Environ.* 408, 563–570.
- González, M.M., Santos, J.L., Aparicio, I., Alonso, E., 2010b. Method for simultaneous determination of the most problematic families of organic pollutants in compost and compost-amended soil. *Anal. Bioanal. Chem.* 397, 277–285.
- Hampel, M., González-Mazo, E., Vale, C., Blasco, J., 2007. Derivation of predicted no effect concentrations (PNEC) for marine environmental risk assessment: application of different approaches to the model contaminant Linear Alkylbenzene Sulphonates (LAS) in a site-specific environment. *Environ. Int.* 3, 486–491.
- HERA, 2009. Human & environmental risk assessment on ingredients of European household cleaning products: linear alkylbenzene sulphonates (Cas No. 68411-30-3). <http://www.heraproject.com/files/48-F-HERA_LAS_Report_28_Version_4_-_June_09%29.pdf> (accessed 21.07.11).
- Krogh, P.H., Lopez, C.V., Cassani, G., Jensen, J., Holmstrup, M., Schraepen, N., Jørgensen, E., Gavor, Z., Temara, A., 2007. Risk assessment of linear alkylbenzene sulphonates, LAS, in agricultural soil revisited: robust chronic toxicity tests for *Folsomia candida* (Collembola), *Aporrectodea caliginosa* (Oligochaeta) and *Enchytraeus crypticus* (Enchytraeidae). *Chemosphere* 69, 872–879.
- Magoarou, P., 2000. Workshop on problems around sludge. Proceedings. European Commission, Joint Research Centre, EUR 19657 EN, p. 13.

- Mann, R.M., Bidwell, J.R., 2000. Application of the FETAX protocol to assess the developmental toxicity of nonylphenol ethoxylate to *Xenopus laevis* and two Australian frogs. *Aquat. Toxicol.* 51, 19–29.
- Pakou, C., Kornaros, M., Stamatelatou, K., Lyberatos, C., 2009. On the fate of LAS, NPEOs and DEHP in municipal sewage sludge during composting. *Bioresour. Technol.* 100, 1634–1642.
- Petersen, S.O., Henriksen, K., Mortensen, G.K., Krogh, P.H., Brandt, K.K., Sørensen, J., Madsen, T., Petersen, J., Grøn, C., 2003. Recycling of sewage sludge and household compost to arable land: fate and effects of organic contaminants, and impact on soil fertility. *Soil Till Res.* 72, 139–152.
- Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environ. Int.* 34, 1033–1049.
- Staples, C.A., Weeks, J., Hall, J.F., Naylor, C.G., 1998. Evaluation of aquatic toxicity and bioaccumulation of C8- and C9-alkylphenol ethoxylates. *Environ. Toxicol. Chem.* 17, 2470–2480.
- TenEyck, M.C., Markee, T.P., 2007. Toxicity of nonylphenol, nonylphenol monoethoxylate, and nonylphenol diethoxylate and mixtures of these compounds to *Pimephales promelas* (Fathead Minnow) and *Ceriodaphnia dubia*. *Arch. Environ. Contam. Toxicol.* 53, 599–606.
- US EPA (United States Environmental Protection Agency) (2005) Aquatic life ambient water quality criteria-nonylphenol. EPA-822-R-05-005. Final report. United States Environmental Protection Agency, Washington, DC.
- Van Vlaardingen, P., Posthumus, R., Traas, T.P., 2003. Environmental Risk Limits for Alkylphenols and Alkylphenol Ethoxylates. National Institute of Public Health and the Environment, report 601501019. Bilthoven, The Netherlands.
- Ying, G.G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environ. Int.* 32, 417–431.
- Yu, Y., Xu, J., Sun, H., Dai, S., 2008. Sediment-porewater partition of nonylphenol polyethoxylates: field measurements from Lanzhou Reach of Yellow River, China. *Arch. Environ. Contam. Toxicol.* 55, 173–179.